university of groningen

University Medical Center Groningen

University of Groningen

# Magnetic interactions and the pressure phase diagram of CuGeO3

van Loosdrecht, P.H.M.; Zeman, J.; Martinez, G.; Dhalenne, G.; Revcolevschi, A.

*Published in:*
Physical Review Letters

*DOI:*
10.1103/PhysRevLett.78.487

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

*Document Version*
Publisher's PDF, also known as Version of record

*Publication date:*
1997

Link to publication in University of Groningen/UMCG research database

*Citation for published version (APA):*
van Loosdrecht, P. H. M., Zeman, J., Martinez, G., Dhalenne, G., & Revcolevschi, A. (1997). Magnetic interactions and the pressure phase diagram of CuGeO3. *Physical Review Letters*, *78*(3), 487 - 490. https://doi.org/10.1103/PhysRevLett.78.487

**Copyright**
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

**Take-down policy**
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

*Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.*

Download date: 05-05-2023

# Magnetic Interactions and the Pressure Phase Diagram of $CuGeO_3$

P. H. M. van Loosdrecht,* J. Zeman,† and G. Martinez

*Grenoble High Magnetic Field Laboratory, Max-Planck-Institut für Festkörperforschung and Centre National de la Recherche Scientifique, 25 Avenue des Martyrs, BP 166, F-38042 Grenoble Cedex 9, France*

G. Dhalenne and A. Revcolevschi

*Laboratoire de Chimie des Solides, Univerité de Paris-Sud, Bâtiment 414, F-91405 Orsay, France*

(Received 23 September 1996)

A pressure and temperature dependent Raman study of the vibrational and spin dynamics in $CuGeO_3$ is presented. A new low temperature, high pressure phase has been identified, and a pressure-temperature phase diagram is proposed for $CuGeO_3$. The pressure dependence of the effective exchange interaction, of the spin-Peierls gap and of the spin-Peierls temperature, strongly supports a model in which next-nearest-neighbor interactions stabilize the spin-Peierls ground state. The Raman data allow for a quantitative estimate of the pressure dependence of the next-nearest-neighbor interactions. [S0031-9007(96)02194-1]

PACS numbers: 62.50.+p, 75.30.Et, 75.40.Gb, 78.30.–j

The discovery of the first inorganic compound showing the spin-Peierls (SP) transition, $CuGeO_3$, has sparked an active research into the physics and properties of this quasi-one-dimensional magnetoelastic $S = 1/2$ Heisenberg antiferromagnet [1–4]. The first evidence for a SP transition in $CuGeO_3$ came from the observation of the characteristic exponential vanishing of all components of the magnetic susceptibility below $T_{sp} \approx 14$ K [1]. Shortly after, inelastic neutron scattering (INS) and x-ray diffraction confirmed the SP transition by the observation of the opening of a gap in the magnetic excitation spectrum, and the associated dimerization of the lattice [5–7]. It is now well established that the ($H$-$T$) phase diagram of $CuGeO_3$ conforms to the standard SP behavior, i.e., a uniform phase above $T_{sp}$, a spin-Peierls or dimerized phase below $T_{sp}$, and a modulated phase at high magnetic fields [$T < T_{sp}(H)$] [8].

Although $CuGeO_3$ appears to be a good example of a standard SP system, there are several problems which remain open at present. One of these is the observation that above $T_{sp}$ the magnetic susceptibility $\chi(T)$ strongly deviates [1] from the usual Bonner-Fisher behavior [9] expected for a one-dimensional $S = 1/2$ Heisenberg antiferromagnet. This deviation can have several origins such as strong spin-phonon interactions, interchain interactions (about 10% of the intrachain interaction [5]), or next-nearest-neighbor (nnn) interaction. For the latter it has already been shown [10,11] that this may explain both $\chi(T > T_{sp})$ as well as the observed dispersion for the magnetic excitations in the dimerized phase. Moreover, these studies estimate that the nearest-neighbor (nn) interaction is substantially higher ($J_{nn} \sim 150$–$170$ K [10,11]) than earlier determinations from $\chi(T)$ [1] and INS [5] data ($J_{nn} \sim 90$–$120$ K), in good agreement with the result $J_{nn} \approx 180$ K obtained from high field Faraday rotation experiments [12]. Since a frustrated spin chain with $\alpha = J_{nnn}/J_{nn} \geq \alpha_c \sim 0.24$–$0.3$ [10] has a spin gap and a singlet ground state—even without spin-phonon interactions—it is very likely that not only spin-phonon interactions, but also the nnn interactions in $CuGeO_3$ play an important role in stabilizing the SP ground state. This is also in good agreement with recent magnetostriction and thermal expansion experiments [13].

Another problem which remains open at present is the existence of a soft mode. Despite serious efforts [14], the soft mode predicted by standard SP theory [15,16] has so far not been detected in $CuGeO_3$. Though this might be due to a weak intensity of the concerned phonon in INS experiments, its apparent absence raises serious doubts about the nature of the phase transition itself.

The structure of $CuGeO_3$ consists of flat $CuO_4$ and tetrahedral $GeO_4$ units, which form chains running along the orthorhombic $c$ axis [space group $Pbmm$ [17]; see Fig. 1(a)]. The magnetic chains are formed by the $Cu^{2+}$ ions of the $CuO_4$ units, with a nn exchange path running over the Cu-O(2)-Cu bonds. The intrachain frustration is thought to be due to superexchange over Cu-O(2)-O(2)-Cu paths [10].

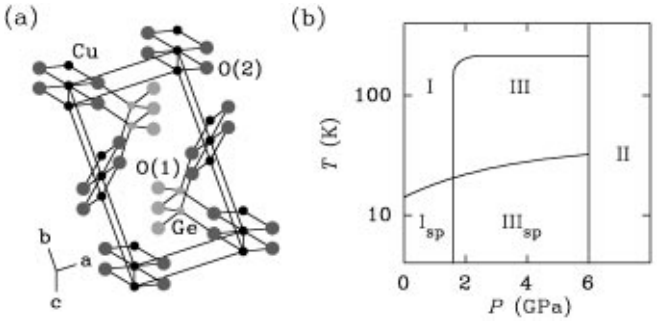


FIG. 1. (a) Crystal structure of $CuGeO_3$. (b) Proposed schematic ($P$-$T$) phase diagram of $CuGeO_3$.

 © 1997 The American Physical Society 

In view of the pronounced magnetoelastic properties of $CuGeO_3$, a study of the vibrational and magnetic excitations under hydrostatic pressure provides an attractive method to obtain a better understanding of the interplay between phonons and magnetic excitations in $CuGeO_3$. Previous experiments have shown that $CuGeO_3$ undergoes a phase transition from the orthorhombic *Pbmm* phase I at atmospheric pressure to a, presumably monoclinic, phase II at ~6–7 GPa [18]. More recently, it has been proposed that this transition might be due to intercalation of the methanol/ethanol pressure medium [19], though subsequent experiments [20] have shown this to be unlikely. A remarkable observation is the huge 20% decrease of the *b* axis dimension at the first order I-II phase transition, demonstrating the strong pressure sensitivity of the $CuGeO_3$ lattice. In addition, recent experiments have shown that the magnetic properties of $CuGeO_3$ are also quite sensitive to pressure. INS [21] results have demonstrated a strong positive pressure coefficient for the SP gap energy, whereas susceptibility experiments [22] have shown a strong increase of $T_{sp}$ upon increasing pressure. This is in good agreement with earlier predictions [23,24], but difficult to understand in terms of the standard SP theories [15,16] and the structural changes in $CuGeO_3$ upon increasing pressure [25].

The present Letter reports on a detailed study of the vibrational and magnetic properties of $CuGeO_3$ as a function of pressure and temperature using Raman spectroscopy. The results obtained on vibrational scattering are used to propose a pressure-temperature phase diagram. The observed behavior of the magnetic scattering gives strong evidence that nnn interactions in fact drive the SP transition in $CuGeO_3$. It allows for an evaluation of the pressure dependence of these interactions.

Raman experiments have been performed using a clamp type diamond anvil cell. The cell has been mounted in a He flow cryostat with a temperature regulation better than 1 K. Figure 2 displays some representative Raman spectra recorded at $T = 7$ K in a (ZZ) geometry at various pressures between 0 and 7 GPa, using either methanol/ethanol or Ar as a pressure medium. Here, (ZZ) indicates the polarization of the incoming and scattered light parallel to the chains direction. The two modes around 185 and 330 $cm^{-1}$, observed in all spectra below 6 GPa, are due to $A_g$ phonons of the orthorhombic structure. The typical Raman features [26–28] of the SP phase (phase $I_{sp}$) can be observed in the atmospheric pressure spectrum (bottom curve): the sharp peak at $E_{min} = 30$ $cm^{-1}$, the broad two magnon maximum at $E_{max} = 230$ $cm^{-1}$, and the magnetically activated phonon modes at 107 and 370 $cm^{-1}$, where the former is strongly Fano distorted due to spin-phonon interaction [27]. Upon increasing pressure the energy of the 30 $cm^{-1}$ mode, which is observed up to 4.4 GPa, shows a rapid increase, whereas a slight decrease is found for the two magnon peak energy.

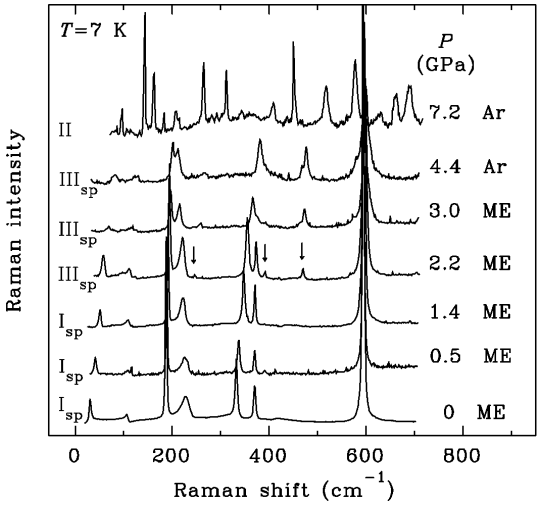


FIG. 2. Partially polarized (ZZ) Raman spectra of $CuGeO_3$ at $T = 7$ K for various pressures. The pressure media (ME: methanol/ethanol; Ar: argon) used are indicated on the right side, and the different phases on the left side.

Goñi *et al.* [20] have proposed a $(T, P)$ phase diagram for $CuGeO_3$, based on Raman experiments in a He filled diamond anvil cell. Since the results obtained here are slightly different, we start with a brief discussion of the phases, and phase diagram observed in this study. At atmospheric pressure and ambient temperature $CuGeO_3$ has a transparent light blue appearance and an orthorhombic crystal structure. Its first order Raman spectrum shows, as expected, a total of 12 active modes in the various geometries [29]. The crystals used in this study, grown by a floating zone technique [30], did not show any deviation from the selection rules, indicating a good crystal quality. Up to 6 GPa the crystals remain in the *Pbmm* phase, and all Raman active phonon modes show a positive pressure coefficient.

The first order I-II phase transition is evidenced by the drastic changes in the Raman spectrum (compare Fig. 2 bottom and top curves). This new phase, which has a transparent green appearance, is believed to be monoclinic [18], and is probably accompanied by a cell doubling in at least one direction. The observation of this phase transition is in good agreement with earlier results [18–20].

In contrast to earlier results [19] we have observed the I-II phase transition also with Ar as pressure medium. In this case, however, the phase transition does not occur immediately. Between 6 and 7 GPa we observed a coexistence of phase II with another phase which appears dark blue in color. A comparison of the Raman spectrum obtained for this phase with earlier results shows that this phase is in fact phase IIa of Ref. [20]. Above 7 GPa the whole sample has transformed to the light green phase II. This slightly different phase sequence observed when using Ar as a pressure medium is most likely due to the huge contraction of the *b* axis at the I-II phase transition,

which is evidently less easily achieved in a van der Waals solid as compared to a liquid pressure medium. The observation of the I-II transition using Ar, however, does once more demonstrate that phase II cannot be due to intercalation of alcohols [19].

Goñi *et al.* reported the existence of a high pressure phase (phase Ib; $T < 180$ K, $3 < P < 6$ GPa [20]), characterized by the appearance of two new lines, at 150 and 300 $cm^{-1}$, in the Raman spectrum and the disappearance of the SP transition. In samples used in the present study we could not observe the I-Ib phase transition. Instead a different phase transition is observed at $T \approx 215$ K for $1.6 < P < 6$ GPa to a new phase (phase III), characterized by the appearance of several new lines, at 247, 393, and 471 $cm^{-1}$, in the Raman spectrum (see arrows in Fig. 2). A remarkable observation is that the SP transition is apparently not influenced by the I-III transition, as evidenced by the appearance of all Raman modes of the SP phase. In fact, we did not observe any discontinuities upon going from phase $I_{sp}$ to phase $III_{sp}$. This leads to the conclusion that the I-III phase transition involves only a small distortion of the crystal structure, in good agreement with the observation of only a few new Raman lines in phase III. To conclude the discussion on the different phases in $CuGeO_3$ Fig. 1(b) proposes a schematic $(P, T)$ phase diagram for $CuGeO_3$. The major differences with the phase diagram proposed in Ref. [20] are the presence of phase III (and absence of phase Ib), and the observation of the SP transition up to at least 4.4 GPa (phase $I_{sp}$ and $III_{sp}$). We do not believe that the origin of these differences is due to nonhydrostaticity, since here, as well as in Ref. [20], no evidence of this is found, at least below 2.5 GPa. But, since the phase sequence is apparently sensitive to the pressure medium (i.e., hydrostaticity), it is not unlikely that the presence of defects may change this sequence.

We now turn to the pressure dependence of the magnetic scattering. The energy of the 30 $cm^{-1}$ mode is highly sensitive to pressure, as shown in Fig. 3(a). The straight line through the data corresponds to $E_{\min}[\mathrm{cm}^{-1}] = 31.6 + 11P[\mathrm{GPa}]$. For comparison Fig. 3(a) also shows the pressure dependence of twice the SP gap as derived from INS experiments [21]. Clearly the Raman mode does not correspond to twice the energy gap, as has been assumed earlier [27,28,31]. Rather, we believe that this deviation gives clear evidence for the existence of the two-magnon bound state [26], with a strongly pressure dependent binding energy ($\sim 2$ $cm^{-1}$ at 0 GPa, and $\sim 15$ $cm^{-1}$ at 4.4 GPa). This conclusion limits the interpretation of the Raman spectrum in terms of frustration alone [32]. Based on the present results one may say that the magnetic Raman response in the SP phase is a superposition of this bound state and a weighted two- or three-dimensional spin density of states [26–28]. The exact nature of the scattering mechanism, however, remains unclear at present. The usual exchange scattering mechanism [33] is unable to explain the observed magnetic Raman activity [32], indicating that additional mechanisms, such as spin-phonon interactions, need to be included to obtain a full understanding of the Raman spectrum of $CuGeO_3$.

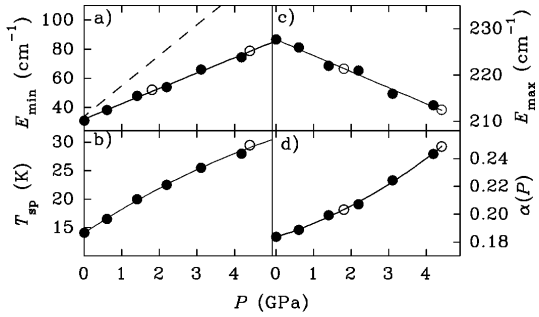


FIG. 3. Pressure dependence of (a) the bound magnon state (symbols) and twice the SP gap (dashed line, Ref. [21]) (b) the spin-Peierls transition temperature, (c) the energy of the two-magnon maximum in the Raman spectra, and (d) the frustration parameter $\alpha$ (see text). Open symbols refer to experiments using Ar as pressure medium.

The presence of the bound state mode can be used to determine the spin-Peierls transition temperature. The pressure dependence of $T_{sp}$ obtained in this way is plotted in Fig. 3(b). We find a much more linear behavior than reported previously [20]: $T_{sp} = 14 + 4.5P - 0.25P^2$ [Fig. 3(b), solid line]. The pressure dependence of $T_{sp}$ at low pressures is found to be in good agreement with the results from INS and susceptibility experiments [21,22], as well as with predictions from thermodynamic experiments [23,24].

The peak around $E_{max} = 230$ $cm^{-1}$, and the decreasing continuum towards lower energies, originates from two-magnon exchange interaction scattering processes and reflects the magnon density of states [26,27,33]. In systems without frustration, $E_{max}$ gives an estimate of the effective nn exchange energy, provided one makes a first order correction to the energy scale in order to account for magnon-magnon interactions ($E_{max} = 2.7J_{nn}$) [34]. In a frustrated system, however, one should replace $J_{nn}$ by an effective interaction $J_{eff}$, depending both on $J_{nn}$, and $J_{nnn}$. Raman data at atmospheric pressure yield $J_{eff} = 121$ K (10.4 meV), in good agreement with INS data [5]. The pressure dependence of $E_{max}$ is plotted in Fig. 3(c). Though a clear decrease is observed upon increasing pressure, it is much weaker than predicted from INS data [21]. This deviation may result from a pressure dependence of the ratio $\alpha = J_{nnn}/J_{nn}$, which has not been considered in Ref. [21]. The pressure dependent structural changes observed in $CuGeO_3$ [25] mainly involve the bonds in the $b$ direction [Ge-O(2), Cu-O(1)], which presumably play an important role in the nnn interactions. According to Ref. [25], the changes in the length and angle of the O(2)-Cu-O(2) bonds are quite weak. One therefore expects only a weak pressure

dependence of $J_{nn}$, and we are led to assume that the main pressure variation of $\alpha$ is induced by that of $J_{nnn}$.

Using a simple model, one can derive the pressure dependence of $\alpha$ from the position of the two-magnon maximum. The Hamiltonian describing a dimerized linear frustrated spin chain can be expressed as

$$H = \sum_i J_{nn}[1 + \delta(-1)^i]S_iS_{i+1} + J_{nnn}S_iS_{i+2}, \quad (1)$$

where $\delta$ is due to the dimerization. Without dimerization, linear spin-wave theory gives a dispersion relation $E_{\delta=0}(q) = \zeta(q,\alpha)E_0\sin(q)$, with $\zeta(q,\alpha) = \sqrt{1 - 4\alpha[1 - \alpha\sin(q)]}$, $E_0 = (\pi/2)J_{nn}$ the maximum spin excitation energy for $\alpha = 0$, and $q$ the wave vector along the chains. The SP gap $\Delta$ may be introduced phenomenologically by writing

$$E^2(q) = \Delta^2 + [\zeta E_0\sin(q)]^2. \quad (2)$$

In order to estimate $\Delta$, $E_0$, and $\alpha$ at zero pressure we have fitted Eq. (2) to INS data [5,35]. A good fit is obtained for $\Delta = 2.1$ meV, $E_0 = 24.5$ meV ($J_{nn} = 181$ K), and $\alpha = 0.18$. Using Eq. (2), and the pressure dependence $\Delta(P)$ obtained in [21] one may now evaluate $\alpha(P)$. The resulting pressure dependence $\alpha(P)$, plotted in Fig. 3(d), clearly show a pronounced increase of the nnn interactions upon increasing pressure. In obtaining this result the possible pressure dependence of the nn interactions (i.e., $E_0$) has been neglected. However, from structural considerations one would, in fact, expect a small *increase* of $J_{nn}$ upon increasing pressure, which would lead to an even stronger pressure dependence of $J_{nnn}$. We believe that the observed pressure dependence of $J_{nnn}$ is due to the changes in the strong Ge-O(2) bonds [25], which determine the orientation of the oxygen ligands, and hence of the Cu-O(2)-O(2)-Cu superexchange.

In conclusion, based on pressure dependent Raman data we proposed a ($P$-$T$) phase diagram for $CuGeO_3$ which differs from earlier results [20]. In particular a new phase III has been observed which like phase I, also undergoes a SP transition at low temperatures. The comparison of the pressure dependence of the 30 $cm^{-1}$ Raman mode with that of the SP gap clearly shows that the 30 $cm^{-1}$ mode does not reflect the density of states. This leads us to conclude that this mode is due to a two-magnon bound state, which, given the strong pressure dependence of its binding energy, as well as its absence in the uniform phase, is likely induced by the magnetic dimerization. Finally, we have clearly shown that the increase of the SP gap and the SP transition temperature, as well as the decrease of the maximum energy of the spin excitations (i.e., $J_{eff}$) upon increasing pressure has a natural explanation in terms of nnn interactions. From the present results one may conclude that the phonons, though essential for the lattice dimerization, play only a minor role in determining the SP gap and transition temperature in $CuGeO_3$, but that these are largely determined by the ratio of the nn and nnn interactions.

The Grenoble High Magnetic Field Laboratory is a "laboratoire conventionné à l'Université Joseph Fourier de Grenoble."

*Present address: 2. Phys. Institut, RWTH Aachen, Templergraben 55, 52056 Aachen, Germany.
†On leave from the Institute of Physics, Academy of Sciences, Prague, Czech Republic.

[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
[2] J. W. Bray *et al.*, in *Extended Linear Chain Compounds*, edited by J. S. Miller (Plenum Press, New York, 1983), Vol. 3.
[3] J. P. Boucher and L. P. Regnault, J. Phys. I (France) (to be published).
[4] Recently a possible second example of an inorganic SP compound has been reported ($\alpha'$-$NaV_2O_5$); see M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).
[5] M. Nishi, O. Fujita, and J. Akimitsu, Phys. Rev. B **50**, 6508 (1994).
[6] K. Hirota *et al.*, Phys. Rev. Lett. **73**, 736 (1994).
[7] J. P. Pouget *et al.*, Phys. Rev. Lett. **72**, 4037 (1994).
[8] M. Hase *et al.*, Phys. Rev. B **48**, 9616 (1993).
[9] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).
[10] G. Castilla, S. Chakravarty, and V. J. Emery, Phys. Rev. Lett. **75**, 1823 (1995).
[11] J. Riera and A. Dobry, Phys. Rev. B **51**, 16 098 (1995).
[12] H. Nojiri *et al.*, Phys. Rev. B **52**, 12 749 (1995).
[13] B. Büchner *et al.*, Phys. Rev. Lett. **77**, 1624 (1996).
[14] See, for instance, J. E. Lorenzo *et al.*, Phys. Rev. B **50**, 1278 (1994).
[15] E. Pytte, Phys. Rev. B **10**, 4637 (1974).
[16] M. C. Cross and D. S. Fisher, Phys. Rev. B **19**, 402 (1979).
[17] H. Völlenkle, A. Wittman, and N. Nowotny, Monatsh. Chem. **98**, 1352 (1967).
[18] D. M. Adams, J. Haines, and S. Leonard, J. Phys. Condens. Matter **3**, 5183 (1991).
[19] A. Jayaraman *et al.*, Phys. Rev. Lett. **75**, 2356 (1995).
[20] A. R. Goñi *et al.*, Phys. Rev. Lett. **77**, 1079 (1996).
[21] M. Nishi *et al.*, Phys. Rev. B **52**, R6959 (1995).
[22] H. Takahashi *et al.*, Solid State Commun. **95**, 817 (1995).
[23] H. Winkelman *et al.*, Phys. Rev. B **51**, 12 884 (1995).
[24] M. Weiden *et al.*, Z. Phys. B **98**, 167 (1995).
[25] S. Katano *et al.*, Phys. Rev. B **52**, 15 364 (1995).
[26] H. Kuroe *et al.*, Phys. Rev. B **50**, 16 468 (1994).
[27] P. H. M. van Loosdrecht *et al.*, Phys. Rev. Lett. **76**, 311 (1996).
[28] P. Lemmens *et al.*, Physica (Amsterdam) **223B & 224B**, 535 (1996).
[29] S. D. Dević *et al.*, J. Phys. Condens. Matter **6**, L745 (1994).
[30] A. Revcolevschi and G. Dhalenne, Adv. Mater. **5**, 9657 (1993).
[31] I. Loa *et al.*, Solid State Commun. **99**, 231 (1996).
[32] V. N. Muthukumar *et al.*, Phys. Rev. B **54**, R9635 (1996).
[33] P. A. Fleury and R. Loudon, Phys. Rev. **166**, 514 (1968).
[34] K. B. Lyons *et al.*, Phys. Rev. B **37**, 2353 (1988).
[35] L. P. Regnault *et al.*, Phys. Rev. B **53**, 5579 (1996).